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RESEARCH ON MITIGATION OF SPLINE WEAR  
BY MEANS OF LUBRICATION

QUARTERLY PROGRESS REPORT NO. 3  
Contract NOw-65-0224-f

W.D. Weatherford, Jr.  
M.L. Valtierra  
P.M. Ku

to

Bureau of Naval Weapons  
Department of the Navy  
Washington, D.C. 20360

February 15, 1966

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SOUTHWEST RESEARCH INSTITUTE  
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Department of Aerospace Propulsion Research

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APPROVED:



P.M. Ku, Director  
Department of Aerospace  
Propulsion Research

## FOREWORD

This report was prepared at Southwest Research Institute under USN Contract NOw-65-0224-f. The work was administered by the Bureau of Naval Weapons, Department of the Navy, Washington, D.C. 20360, with Mr. S.M. Collegeman serving as project engineer.

This report covers work performed in the period from November 15, 1965, through February 15, 1966.

Acknowledgment is given for comments and suggestions made by Messrs. S.M. Collegeman and C.C. Singleterry of the Bureau of Naval Weapons and Mr. M.J. Devine of the Aeronautical Materials Laboratory, Naval Air Engineering Center. The grease samples studied in this program were provided by Mr. Devine.

## ABSTRACT

This report reviews the third quarter of the third year of a research program on the mitigation of spline wear by means of lubrication.

During this quarter, experiments have included investigations of the effect of hydrocarbon antioxidants on the spline wear observed when operating submerged in mineral oil. The results indicate that certain hydrocarbon antioxidants provide periods of negligible wear which otherwise do not occur in air-saturated mineral oil.

The observed antioxidant effect and previously reported influences of environment composition are tentatively interpreted in terms of postulated wear mechanisms.

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## I. INTRODUCTION

Under Contract NOw-65-0224-f, Southwest Research Institute is currently conducting a program of research on the mitigation of spline wear by means of lubrication.

During the first two years of this program, a laboratory method was developed for simulating the wear experienced by misaligned splines. The variables studied as part of this program included spline material, spline environment, spline tooth contact pressure, and misalignment oscillation amplitude. Performance data were obtained for ten greases, three bonded solid-film lubricants, and a vapor-deposited molybdenum metal coating, using dry air, moist air, JP-5, and JP-6 as spline environment fluids. The cumulative results from the first two years of this program were presented in Summary Technical Report, Contract NOw-64-0341-d, SwRI Report No. RS-456, May 13, 1965.

During the present year of this program, the emphasis is shifted toward a "cause and effect" investigation with the objective being to interpret the "how and why" of spline wear and its mitigation. This research effort utilizes the experimental apparatus and specimens developed in the previous portions of the program, with the range of operating conditions being about the same as previously employed. In addition to the study of mechanisms, the program includes a limited number of lubricant evaluations to confirm the relative performance of selected lubricants of interest.

In Quarterly Progress Report No. 2, November 15, 1965, the progress achieved during the second quarter of the current contract was reviewed. It is the purpose of the present report to review the results obtained during the third quarter of this research program. The experimental apparatus and operating procedures employed during this period are the same as those described in previous reports.

## II. EXPERIMENTAL PROGRAM

With the exception of a Grease Q evaluation experiment, using Type 2 (AISI 4130 steel, first batch) specimens, the experimental effort during this report period has been devoted entirely to a study of wear characteristics of Type 2A (AISI 4130 steel, second batch) specimens submerged in mineral oil, both with and without additives. These materials and others referred to in this report are described in the following paragraphs:

### Grease A

This MIL-G-7711A Type grease consists of a smooth homogeneous mixture of mineral or synthetic oil or combinations thereof, with a suitable gelling agent. It is a general purpose aircraft grease intended for use in antifriction bearings, gear boxes, and plain bearings where operation at both low temperature ( $-40^{\circ}\text{F}$ ) and high temperature ( $250^{\circ}\text{F}$ ) may be required.

### Greases E, P, and Q

These greases consist of mineral oil with treated clay thickener and  $\text{MoS}_2$ . They are produced by three different manufacturers.

### Mineral Oil

This oil contains no additives. Its viscosity is 300-310 SUS at  $100^{\circ}\text{F}$ . It is a light-medium grade noncompounded midcontinent base stock.

### Zinc Diamyldithiocarbamate

This additive is compounded as a 50 wt % blend in mineral oil. It is considered as an oxidation inhibitor, metal deactivator, and corrosion inhibitor for lubricating oils and greases.

### Phenyl $\alpha$ Naphthylamine

This aromatic amine additive is known to function as an antioxidant for lubricating oils and greases. It is frequently used in both soap and nonsoap greases. The melting point of the commercial additive is  $133^{\circ}\text{F}$ .

The result of the Grease Q evaluation is presented in Table I along with previously obtained data for Greases E and P. These results indicate that Type 2 specimens display equivalent wear characteristics whether lubricated with Greases E, P, or Q.

Experiments with the spline specimens submerged in oil are made using the same procedures as are used with other environment fluids. The only temporary apparatus modification involved is the removal of the pre-heater coil and the sealing of the overflow outlet. Prior to each experiment, a fixed quantity (about 25 ml) of fresh oil is introduced through a fitting in the base of the specimen retainer housing. This quantity of oil has been selected so that the liquid level is about one centimeter above the upper surface of the outer specimen. The oil inlet fitting is sealed, and the experiment is then conducted without the introduction of additional oil.

Because of the extreme gas-phase turbulence in the vicinity of the oscillating specimen shank and gyrator shaft, the atmosphere above the oil surface within the specimen retainer housing is continuously replenished with atmospheric air even though the heated enclosure surrounding the specimen retainer housing is purged with nitrogen at a low rate as a fire-safety measure. This contrasts with previous experiments with splines in gaseous environments where the forced flow of the environment fluid through the specimen retainer housing prevented the turbulent back-diffusion of atmospheric air into the specimen retainer housing. For the oil environment studies, this continuous atmospheric replenishment was confirmed by sampling of the gases within the specimen retainer housing during experiments. Chromatographic analysis of these samples yielded oxygen contents of about twenty percent.

A series of experiments was conducted with air-saturated mineral oil as the environment fluid. Two different antioxidant additives were investigated during this study in order to determine the influence of such additives on the spline wear mitigation characteristics of mineral oil. Phenyl  $\alpha$  naphthylamine and zinc diamyldithiocarbamate were selected as the antioxidants for this study. Each was used at three to four different concentrations, ranging from  $2 \times 10^{-4}$  to  $4 \times 10^{-2}$  gm mols per liter. The results of these experiments are shown in Figures 1 and 2.

With uninhibited mineral oil, wear commences immediately and proceeds at a relatively constant rate of about  $8 \times 10^{-5}$  inch per hour. Although no period of protection is provided by the mineral oil, this result represents about a twenty-five-fold reduction in wear rate relative to the unlubricated case.

TABLE 1. SUMMARY OF EXPERIMENTAL RESULTS FOR  
TYPE 2 SPECIMENS WITH GREASES E, P, AND Q

Designation	Grease Description	Environment Fluid	
		Dry Air Wear Rate (in. /hr) $\times 10^3$	JP-5 Wear Rate (in. /hr) $\times 10^3$
O	None	1.7*, 1.6*, 1.8	0.26*
E	Original Sample	2.8*, 2.5*	0.28*
P	Formulation Similar to Grease E	3.0*, 2.9*	0.30*
Q	Formulation Similar to Grease E	2.5	--

\*Experimental data obtained during previous report periods.

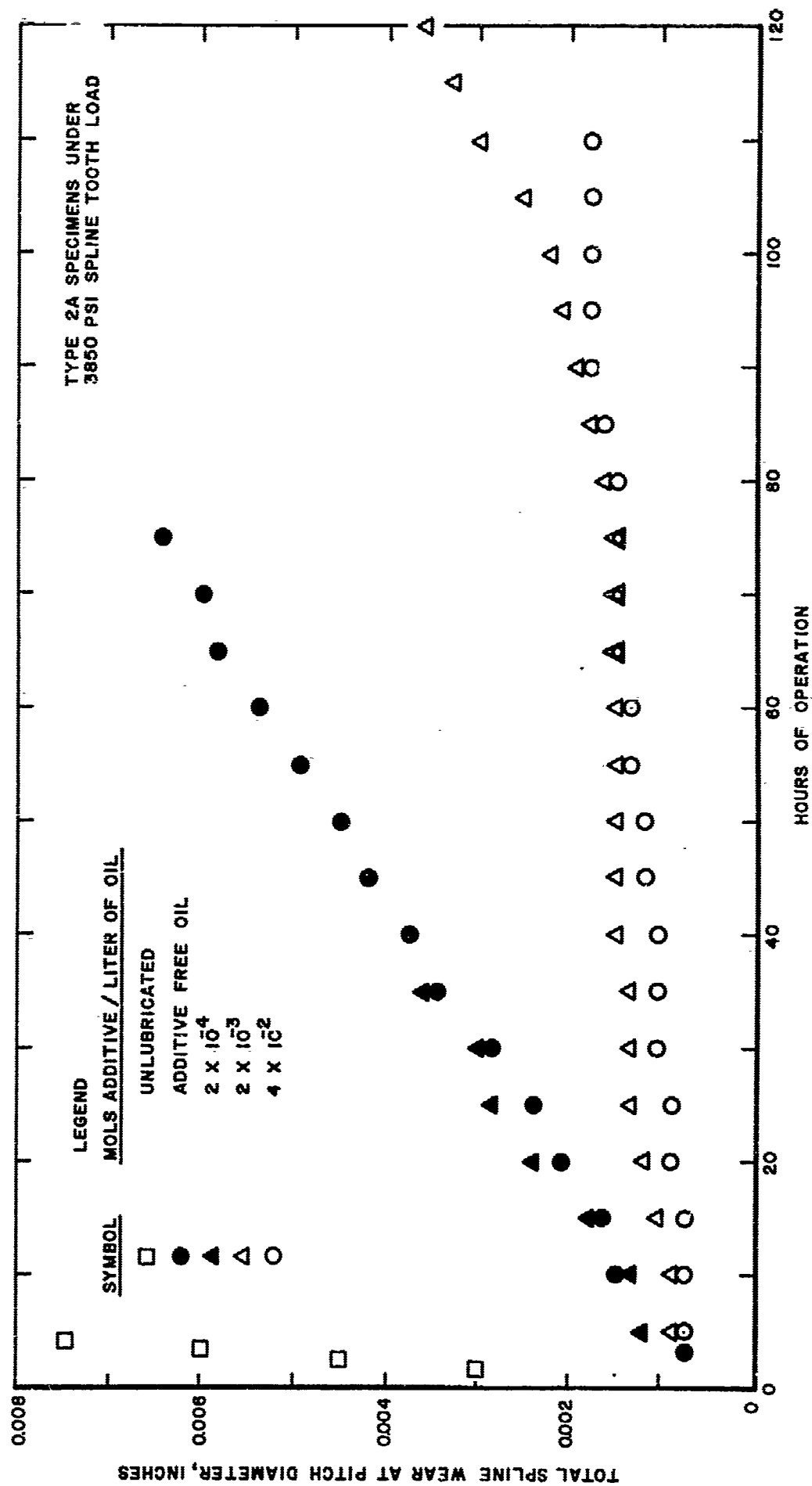


FIGURE 1. INFLUENCE OF ZINC DIAMYLDTHTHIOCARBAMATE ON SPLINE WEAR  
CHARACTERISTICS IN AIR-SATURATED MINERAL OIL

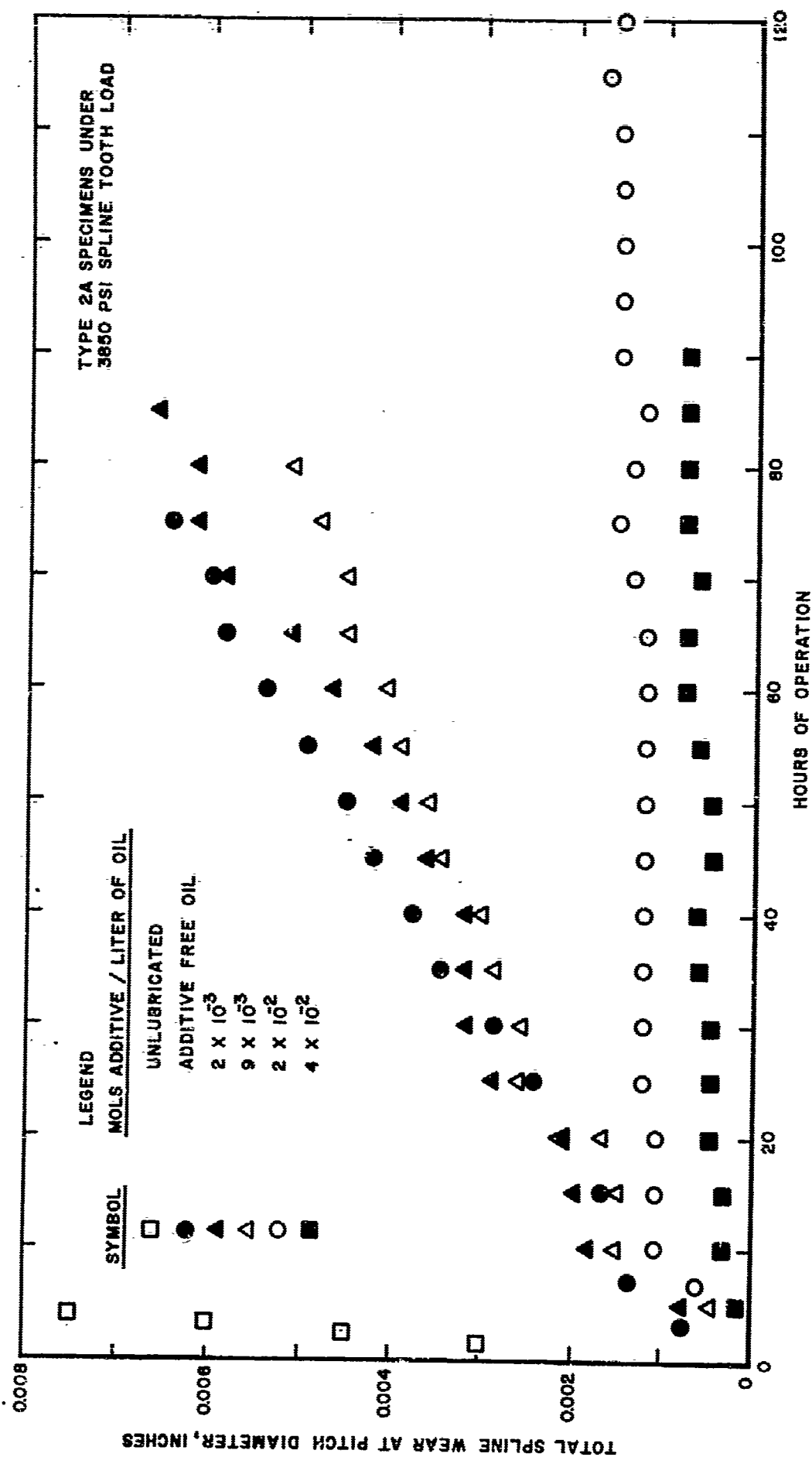


FIGURE 2. INFLUENCE OF PHENYL  $\alpha$  NAPHTHYLAMINE ON SPLINE WEAR  
CHARACTERISTICS IN AIR-SATURATED MINERAL OIL

In the presence of mineral oil containing either of the above additives at a concentration of  $4 \times 10^{-2}$  gm mols per liter, the wear rates are so low that they may be considered negligible, corresponding to those during the period of protection displayed by Grease A. In the case of zinc diamyl-dithiocarbamate, an additive concentration of  $2 \times 10^{-4}$  gm mols per liter did not alter the performance from that of pure mineral oil. On the other hand, as illustrated in Figures 1 and 3, a concentration of  $2 \times 10^{-3}$  gm mols per liter provided a period of protection for about 80-90 hours followed by a steady accelerated wear rate about equivalent to that observed with pure mineral oil. When phenyl  $\alpha$  naphthylamine was used as an additive, concentrations of  $2 \times 10^{-3}$  and  $9 \times 10^{-3}$  gm mols per liter did not significantly alter the performance from that of pure mineral oil. However, as shown in Figures 2 and 3, concentration of  $2 \times 10^{-2}$  gm mols per liter provided an induction period of about 120-130 hours prior to the occurrence of an accelerated wear rate somewhat less than that observed in the unlubricated case.

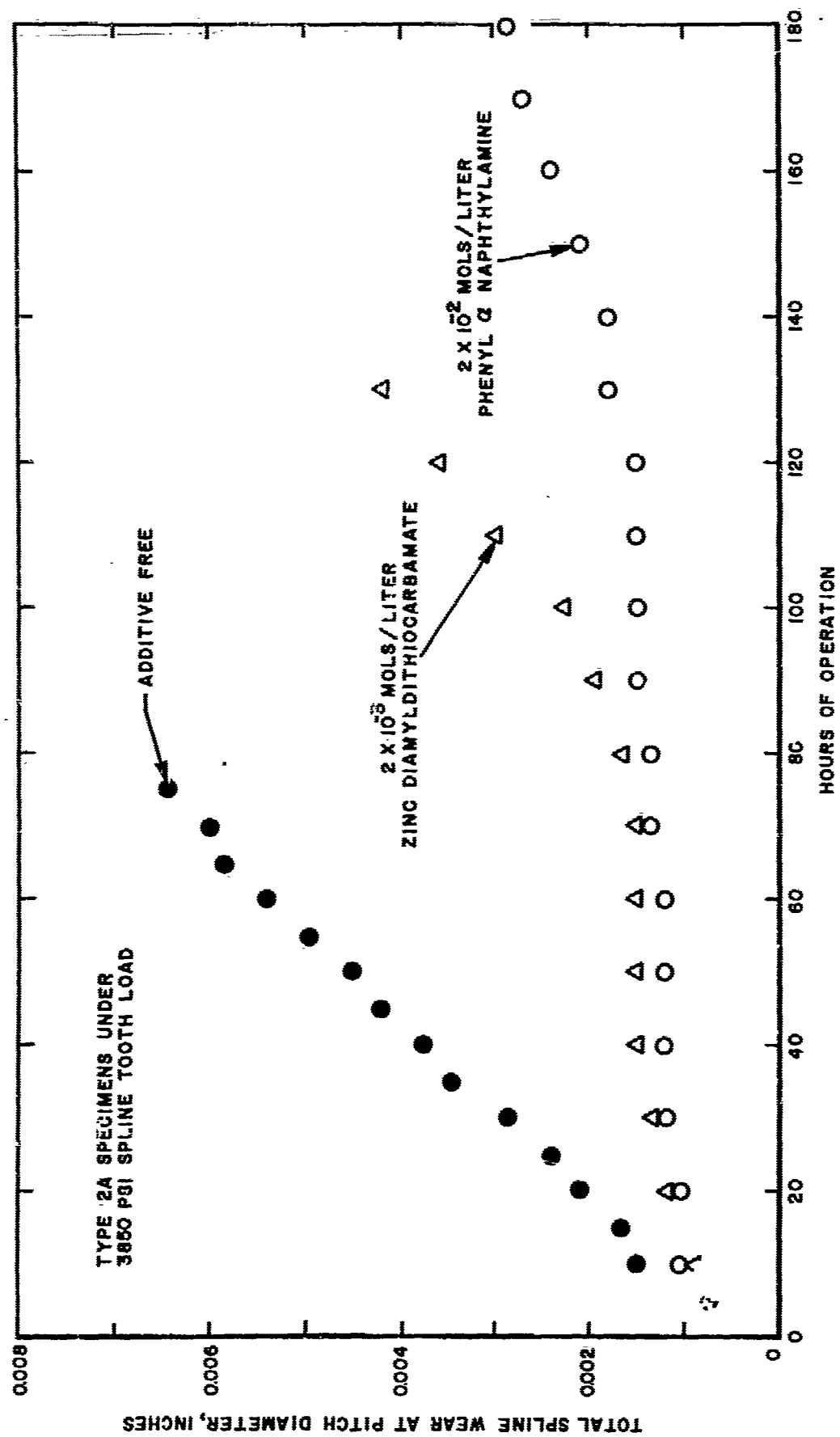


FIGURE 3. COMPARISON OF SPLINE WEAR MITIGATION CHARACTERISTICS OF DIFFERENT ANTIOXIDANTS IN AIR-SATURATED MINERAL OIL

### III. DISCUSSION

The results of the experimental study of spline wear in an air-saturated mineral oil environment, along with previously reported influences of other spline environments, appear to provide additional insight into the mechanism of the wear processes under such conditions. In the presence of uninhibited mineral oil, wear is observed to proceed at a low but steady rate throughout the duration of the experiment. When relatively small quantities of either of two different types of conventional antioxidants are present in the mineral oil, an extended period of negligible wear is observed.

#### A. Spline Wear Mechanisms

In Reference 7, wear rates were measured for a ball oscillating on a flat lubricated with purified mineral oil. Following an extended period of low wear, the wear rate suddenly increased drastically, approaching that of the unlubricated case. This behavior was explained in terms of lubricant displacement by wear debris at the end of the low-wear period. In fact, it was observed that the length of the low-wear period was proportional to the quantity of oil present. Examination of the data of Reference 7 reveals a small but steady wear rate during the period prior to displacement of the oil, and this rate is about twentyfold less than that which occurs immediately following displacement of the oil. These relative magnitudes of the wear rates before and after displacement of the oil are about the same as those observed in the spline wear apparatus operating with and without an air-saturated mineral oil environment. In fact, neither the data of Reference 7 nor those obtained with the spline wear apparatus using pure mineral oil indicate the occurrence of a period of negligible wear such as is consistently observed with some greases.

Previously reported results of this program have shown that the period of negligible wear provided by certain greases may be extended by the use of spline specimens with roughened tooth surfaces. It appears reasonable to associate this induction-period enhancement with the improved grease reservoir capacity of surface cavities. For the sake of discussion, it may be granted that such is the case; however, it now appears that the beneficial effect of the grease may stem from the presence of additives such as hydrocarbon antioxidants, rather than from lubricity alone.

## 1. Wear Processes

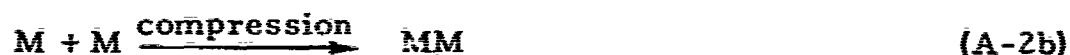
It has been shown that the initial stage of fretting wear in an inert atmosphere proceeds by way of metal transfer between the contacting surfaces without the production of wear debris<sup>(6)</sup>. It has not been established whether fretting wear in the presence of oxygen proceeds by way of oxidation of stressed metal surfaces followed by the formation of debris or by way of the formation of metallic debris followed by oxidation of the debris<sup>(1, 4, 6, 7, 12, 14)</sup>. In either case, the following phenomenological model of the wear processes occurring in splined connections may serve as a tentative basis for interpreting experimental observations. When relative oscillatory motion occurs between the teeth of engaged splines subjected to angular misalignment, localized wear may occur rapidly at certain locations and upon certain teeth until the torsional load is uniformly distributed over the surfaces of all engaged teeth. The occurrence of this initial "wear-in" results from the inherent dimensional tolerances in the spline manufacturing process. Following this "wear-in" period, the asperities on the contacting surfaces continue to be subjected to successive adhesion and fracture by the oscillatory relative motion. The presence of metal oxides or hydroxides, either on the tooth surfaces or in the form of wear debris, alters the nature of the wear processes.

The following physical processes summarize the phenomena which are manifest during fretting wear as metal transfer, debris formation, and boundary lubrication.

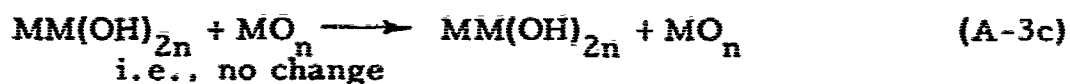
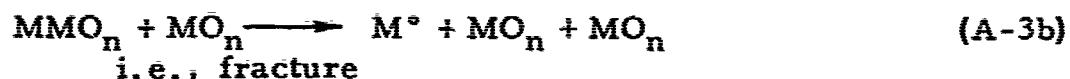
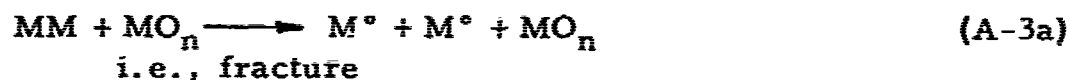
Fracture:



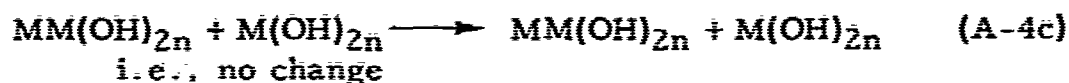
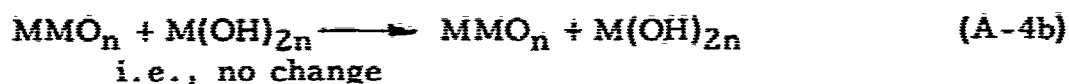
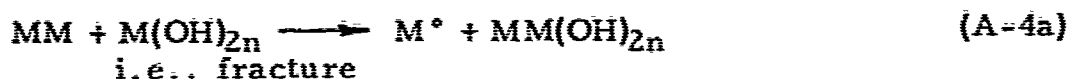
Adhesion:



Oxide abrasion:



Hydroxide abrasion:



where

MM signifies metal bonded to metal (either original bulk phase or adhesion junction)

M\* signifies freshly exposed metal (possibly stress activated) with no chemically bound surface film.

M signifies normal metal surface with chemically bound surface film (possibly oxides or other contaminants)

MO<sub>n</sub> signifies metal oxide surface

MMO<sub>n</sub> signifies metal oxide bonded to metal

M(OH)<sub>2n</sub> signifies metal hydroxide surface

MM(OH)<sub>2n</sub> signifies metal hydroxide bonded to metal

It is evident that, in the above processes, oxides and hydroxides may function as boundary lubricants because their shear strength is significantly less than that of metals. Oxides are generally harder than metals, hence they may contribute substantially to the formation of active metal sites and wear debris (i.e., by way of processes A-3)(1, 4, 6, 7, 12, 14). On the other hand, hydroxides are less abrasive than oxides(4, 14), and they may provide boundary lubrication(1, 7) with the formation of fewer active metal sites and less wear debris (i.e., by way of process A-4a only).

## 2. Lubricant Oxidation

Once active metal sites are formed, their subsequent history is strongly dependent upon the environment to which they are exposed. Therefore, the following discussion of possible lubricant environmental conditions will precede further discussion of the possible fate of active

metal sites. When a hydrocarbon molecule is exposed to oxygen, particularly at elevated temperatures, molecular oxygen is absorbed and converted into chemically combined oxygen which may be much more chemically reactive than molecular oxygen. As oxygen is thus absorbed, hydrocarbons experience oxidative degradation which accelerates as the oxidation proceeds.

The following series of free-radical chemical reactions illustrates accepted mechanisms for the oxidation of hydrocarbons(5, 8, 10, 11, 13).

Peroxy radical chain initiation with molecular oxygen consumption:



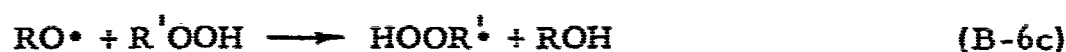
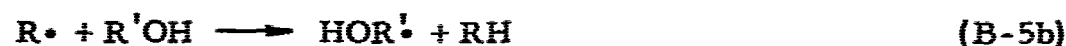
Alkyl radical chain propagation with hydroperoxide formation:



Alkyl radical chain branching with hydroperoxide consumption:



Chain propagation without hydroperoxide formation or consumption:



where

H represents a combined hydrogen atom

R and R' represent hydrocarbon structures or combined hydrogen atoms

O represents a combined oxygen atom

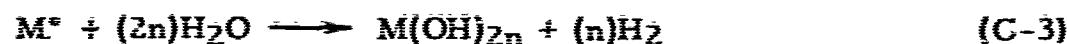
R• and R'• represent carbon-bond free radicals or free hydrogen atoms (e.g., HOR•, HOOR•, etc., may also be represented by R•)

O• represents an oxygen-bond free radical

•OO• represents activated molecular oxygen

### 3. Metal Oxidation

As active metal sites are formed on spline tooth surfaces or on debris particles, one or more of the following oxidation reactions (depending upon the composition of the environment) may proceed rapidly:



Although hydrocarbon free radicals may also participate in the foregoing metal oxidation reactions, their concentrations are negligible relative to those of the electronically stable components. Consequently, the magnitude of the contribution of such reactions should be negligible.

In the presence of water molecules, the following hydration reaction may also occur:

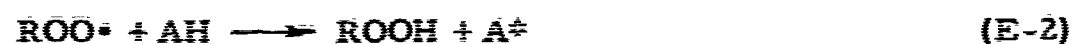


### 4. Role of Lubricant Antioxidants

It is generally recognized that hydrocarbon antioxidants may function according to at least three different mechanisms<sup>(2, 8, 10, 11, 13)</sup>.

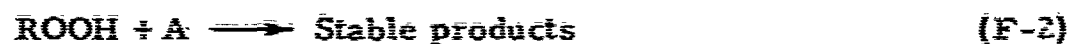
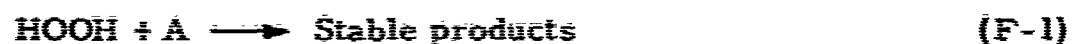
One class of antioxidants simply serves to destroy the oxidative catalytic activity of metal contaminants. The other two classes inhibit the accumulation of hydrocarbon hydroperoxides by interfering with the previously-described free-radical chain reactions.

One of the latter classes of antioxidants functions as an efficient free-radical consumer as illustrated by the following reactions:



where AH represents a free-radical-consumer antioxidant molecule and A\* represents a relatively nonreactive free-radical form of the antioxidant. As indicated by the foregoing reactions, such antioxidants participate in the formation of hydroperoxides while terminating the free-radical chain and consume other free radicals without propagating the chain.

The third class of antioxidant reduces the free-radical chain-branching reactions by decomposing hydroperoxides without the generation of free radicals. This action is indicated by the following reactions:



where A represents a peroxide-decomposer antioxidant molecule.

## B. Interpretation of Observed Spline Wear Phenomena

The observed influence of spline lubricants and environment composition may be interpreted as follows, at least tentatively, in terms of the foregoing phenomenology.

### 1. Influence of Atmosphere Composition

In Quarterly Progress Report No. 1, August 15, 1965, a summary of observed oxygen and moisture influences was presented. This information is reproduced (with one correction) in Table 2 (reexamination of the data indicated that, within the known experimental repeatability, the effect of moisture on the wear rate of unlubricated Type 2A specimens operating in an air environment was not significant). The tabulated

TABLE 2. INFLUENCE OF ENVIRONMENT FLUID COMPOSITION ON SPLINE WEAR PERFORMANCE

Specimen Type	Environment Fluid	Lubricant	Variable	Effect* of Variable on:	
				Induction Period	Steady Wear Rate
2A	Dry	None	With and without Oxygen	No Induction Period	O <sub>2</sub> Detrimental
2A	Moist	None	With and without Oxygen	No Induction Period	O <sub>2</sub> Beneficial
2A	Dry	Grease A	With and without Oxygen	O <sub>2</sub> Detrimental	O <sub>2</sub> Detrimental
2A	Moist	Grease A	With and without Oxygen	O <sub>2</sub> Detrimental	O <sub>2</sub> Detrimental
2A	N <sub>2</sub>	None	With and without Moisture	H <sub>2</sub> O Detrimental	H <sub>2</sub> O Detrimental
2A	Air	None	With and without Moisture	No Induction Period	No H <sub>2</sub> O Effect
2A	N <sub>2</sub>	Grease A	With and without Moisture	H <sub>2</sub> O Beneficial	H <sub>2</sub> O Detrimental
2A	Air	Grease A	With and without Moisture	H <sub>2</sub> O Beneficial	No H <sub>2</sub> O Effect
1	Air	None	With and without Moisture	No Induction Period	H <sub>2</sub> O Beneficial
1	Air	Grease A	With and without Moisture	H <sub>2</sub> O Beneficial	H <sub>2</sub> O Beneficial

\*Experimental data obtained during previous report periods.

influences reveal that the presence of dry oxygen is detrimental to the wear rates of both lubricated and unlubricated Type 2A specimens, in agreement with reactions C-1, 2 and processes A-3. For unlubricated specimens, the presence of moist oxygen is either beneficial or has no significant effect. This result suggests that for unlubricated specimens, extensive formation of hydroxides by reaction C-3 may lead to boundary lubrication by way of processes A-4. In the case of the grease-lubricated specimens, moisture does not appear to protect the splines from the detrimental effects of oxygen (processes A-3). However, for the grease-lubricated specimens in the presence of oxygen, moisture does diminish this detrimental action of oxygen. The latter observations suggest that the formation of hydroxide boundary lubricant by reaction C-3 is possibly limited by low solubility of water vapor in the grease lubricant.

In the absence of oxygen and moisture, metal transfer processes A-1 and A-2 predominate, resulting in low wear and high friction, particularly for unlubricated specimens, but also to some extent for grease-lubricated specimens. Unlubricated specimens in the absence of oxygen and moisture represent the only observed case of an induction period in the absence of a grease lubricant. The addition of oxygen alone is detrimental (by way of processes A-3) for both unlubricated and lubricated specimens, and the addition of water vapor alone is detrimental in both cases except that it improves the induction period of grease-lubricated specimens.

Although this moisture effect in the absence of oxygen appears spurious, it may be explained as follows. Under the metal transfer conditions existing for unlubricated specimens in the absence of oxygen, the true relative slip is increased and adhesion processes (A-2) are inhibited by the characteristics of hydroxides formed by reaction C-3. Accordingly, the resulting increase in wear rate apparently more than offsets any benefit of the hydroxide boundary lubricant. In the case of grease-lubricated specimens in the absence of oxygen, the formation of hydroxides in the presence of moisture appears to provide limited boundary lubrication, thereby improving the induction period. However, the processes occurring between the spline teeth and metallic debris present during the accelerated wear following the induction period appear to be influenced by hydroxides in a manner similar to that of the unlubricated case, leading to a detrimental effect of moisture.

## 2. Influence of Lubricant Antioxidants

The results of experiments conducted with spline specimens submerged in mineral oil clearly demonstrate that hydrocarbon antioxidants may influence spline wear phenomena in the presence of mineral oil.

The two antioxidants were selected to represent free-radical consumers and peroxide decomposers. These different classes of antioxidants are illustrated by reactions E-1, 2, 3 and F-1, 2, respectively. Both of these antioxidants have been employed in conventional greases to protect mineral oil from oxidative deterioration.

Phenyl  $\alpha$  naphthylamine is known to be an effective oxidation inhibitor<sup>(3, 8)</sup>, serving primarily as a free radical trap which consumes peroxy radicals without continuing the chain reaction (reactions E-1, 2, 3). It also functions as a weak peroxide decomposer<sup>(3)</sup>, thereby weakly retarding free-radical chain branching reactions (reactions B-4). The ability of this antioxidant to serve as a free-radical consumer has been confirmed by electron paramagnetic resonance experiments<sup>(9)</sup> where the half-life of the antioxidant radical product (A\* of reactions E-1, 2, 3) was observed to be about thirty hours at 25°C.

Zinc diamyldithiocarbamate and related compounds are known to function primarily by ionically decomposing peroxides<sup>(2)</sup>, thereby preventing free-radical chain branching reactions (reactions B-4). This class of antioxidants also appears<sup>(8)</sup> to function weakly as free-radical consumers (reactions E-1, 2, 3).

The experimental data presented in Figures 1, 2, and 3 indicate that, on a molar basis, zinc diamyldithiocarbamate is about ten times as effective as phenyl  $\alpha$  naphthylamine for protecting splines from wear. A zinc diamyldithiocarbamate concentration of  $2 \times 10^{-3}$  mol per liter yielded an induction period almost as long as did a phenyl  $\alpha$  naphthylamine concentration of  $2 \times 10^{-2}$  mol per liter. An amine concentration of  $2 \times 10^{-3}$  mol per liter did not alter the wear rate appreciably from that of the uninhibited oil. It is of interest to note that experimental data in the literature provide a striking analogy of this effect. When these two classes of antioxidants are used in mineral oil at 340°F, on a molar basis, about ten times as much amine as dithiocarbamate is required to provide equivalent oxidation induction periods<sup>(8)</sup>.

The results of this study reveal that hydrocarbon antioxidants may provide periods of negligible wear which otherwise would not occur for splines operating in air-saturated mineral oil. The indicated correlation between protection from wear and protection from oil oxidation strongly suggests that, in a mineral oil environment, metal oxidation proceeds by preferential reaction with hydroperoxides rather than with dissolved molecular oxygen.

Previously reported results for various grease samples have shown that all of those greases which exhibited significant induction periods

contained antioxidants, and none of those greases which did not exhibit substantial induction periods contained antioxidants. These results may have been coincidental since processes other than the lack of oxidation may contribute to the induction-period phenomena. For example, no study has yet been made of the mechanism of spline wear in the presence of corrosion inhibitors, diester lubricants, or various grease-gelling agents.

#### IV. FUTURE PLANS

The mechanism study will be continued, and sufficient additional confirmatory experiments will be conducted to provide an indication of the most appropriate spline greases for service in air and in JP-5 fuel environments. Experiments will be conducted with mineral oil containing other additives and with specially formulated grease samples in order to extend the study of lubricant additives.

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